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(54) Title: HIGH PURITY NIOBIUM AND PRODUCTS CONTAINING THE SAME, AND METHODS OF MAKING THE SAME

(57) Abstract: High purity niobium metals and alloys containing the same are described. The niobium metal preferably has a purity of at least 99.99 % and more preferably at least 99.999 %. In addition, niobium metal and alloys thereof are described, which either have a grain size of about 150 microns or less, or a texture in which a (100) intensity within any 5 % increment of thickness is less than about 30 random, or an incremental log ratio of (111):(100) intensity of greater than about -4.0, or any combination of these properties. Also described are articles and components made from the niobium metal which include, but are not limited to, sputtering targets, capacitor cans, resistive film layers, wire, and the like. Also disclosed is a process for making the high purity niobium metal which includes the step of reacting a salt-containing niobium and a metal salt along with at least one compound capable of reducing the salt-containing niobium to niobium and in a reaction container. The reaction container or liner in the reaction container and the agitator or liner on the agitator are made from a metal material having the same or higher vapour pressure of melted niobium. The high purity niobium product preferably has a fine and uniform microstructure.

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HIGH PURITY NIOBIUM AND PRODUCTS CONTAINING THE SAME, AND METHODS OF MAKING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to metals, in particular niobium, and products made from niobium metals as well as methods of making and processing the niobium metals.

In industry, there has always been a desire to form higher purity metals for a variety of reasons. With respect to niobium, higher purity metals are especially desirable due to niobium's use as a barrier material for superconductors, as a sputtering source for optical coatings, and for its potential use in electrical components such as capacitors. Furthermore, there is growing interest in high purity niobium-tantalum alloys for use in superconductor filaments, anti-reflective coatings, and possibly as a barrier film for copper interconnects in integrated circuits. Thus, impurities in the metal can have an undesirable effect on the properties and/or the performance of the articles formed from the niobium.

Niobium is found in nature almost exclusively in the form of an oxide (Nb2O5) as columbite ore or as a by-product of the benefaction of tantalum ores. The process used to produce high purity niobium metal typically consists of a chemical extraction and crystallization operation to yield a niobium-bearing ionic salt, a reduction of the ionic salt to produce a niobium metal consolidate, and vacuum melting of the consolidate to produce a high-purity niobium ingot. The vacuum-cast niobium ingot can then be mechanically worked into a variety of mill forms such as sheet, strip, bar, rod, and wire. The high purity niobium ingot and mill forms can also be hydrided, crushed, dehydrided, and subsequently processed to produce niobium powder suitable for capacitor or other powder metallurgy products.

The impurity elements in niobium can be classified as refractory metal impurities, other metallic impurities, and interstitial impurities. Refractory metal impurities include elements such as tantalum, molybdenum, and tungsten; these elements are infinitely soluble

in, and have a similar vapor pressure as niobium and cannot be readily removed through vacuum melting. Therefore, refractory metal impurities must be removed prior to or during the niobium consolidation step using methods such as liquid-liquid extraction, fused salt electrolysis, and chemical vapor deposition (CVD) from niobium halides. Other metallic and interstitial impurities can be removed by vacuum melting of niobium. Metallic elements such as alkali, transition, and rare earth metals have higher vapor pressures and are volatized by vacuum melting processes such as Electron Beam (EB) melting, Vacuum Arc Melting (VAM), Vacuum Arc Remelting (VAR), or Electron Beam Float Zone Melting (EBFZM).

Interstitial impurities (nitrogen, oxygen, carbon, and hydrogen) are also removed by vacuum melting, or by annealing the niobium metal at a high annealing temperature in a strong vacuum. Hydrogen typically is readily outgassed from nitrogen at temperatures above about 400°C in vacuum. Dissolved nitrogen (N) is removed from niobium as diatomic nitrogen (N_2); the kinetics of the reaction is a function of the equilibrium concentration of nitrogen in the niobium as determined by Sievert's law, (E. Fromm and G. Hörz, *Intern. Met. Rev.*, 25 (1980), pp. 269-311, incorporated in its entirety by reference herein).

$$c_N = \sqrt{p_{N_2}} \exp(\Delta S_N^0 / R) \exp(-\Delta H_N^0 / RT)$$

where $\Delta S_N^0 = -70.3 J/mol \bullet K$ and $\Delta H_N^0 = -178 kJ/mol$

Niobium can be decarburized with oxygen either dissolved in the metal or from the atmosphere to form carbon monoxide. The equilibrium concentration of carbon can be estimated for *in-situ* or atmospheric decarburization as follows, (E. Fromm and H. Jehn, *Met. Trans.*, 3 (1972), pp. 1685-1692 and E. Fromm and H. Jehn, *Z. Metallkd.*, 58 (1968), pp. 65-68, incorporated in their entireties by reference herein).

For *in-situ* decarburization $x_{[C]} = \frac{p_{CO}}{p_{O_2}} \exp(-5600/RT - 11.2)$

For atmospheric decarburization $x_{[C]} = \frac{p_{CO}}{p_{O_2}^{1/2}} \exp(-12750/RT - 5.30)$

Typically, carbon is reduced in niobium by assuring that there is a stoichiometric amount or excess of oxygen to completely convert carbon to carbon monoxide. Any remaining oxygen is removed in the form of niobium suboxides by heating at near or above the melting point of niobium within a very high vacuum.

In using a combination of the above-mentioned processes, the ability to produce niobium metal having a purity of 99.999% and better has been demonstrated, (A. Koethe and J.I. Moench, *Mat. Trans., JIM,* **41** No. 1 (2000), pp. 7-16, incorporated in its entirety by reference herein). These or similar methodologies also have been utilized to manufacture tantalum metal having 99.999% purity, (International Application No. WO 87/07650 and European Patent Application No. EP 0 902 102 A1, incorporated in their entireties by reference herein). The ability to produce both high purity niobium and tantalum lends to the creation of techniques for the manufacture of high purity niobium-tantalum alloys.

However, chemical purity is not the lone parameter critical to the functionality and performance of high purity Nb or Nb-Ta alloys. There is a desire to have a high purity Nb or Nb-Ta product having higher purity, a fine grain size, and/or a uniform texture. Qualities such as fine grain size and homogeneous texture can be an important property for superconductor barrier sheets where formability is paramount and for sputtering targets where a uniform microstructure void of (001) localized texture bands can lead to improved uniformity of thickness of the sputtered deposited film. Further, other products containing the niobium having fine grain size can lead to improved homogeneity of deformation and enhancement of deep drawability and stretchability which are beneficial in making capacitors cans, laboratory crucibles, and increasing the lethality of explosively formed

penetrators (EFP's). Uniform texture in tantalum containing products can increase sputtering efficiency (e.g., greater sputter rate) and can increase normal anisotropy (e.g., increased deep drawability), in preform products, (C.A. Michaluk, D.B. Smathers, and D.P. Field, Proc. 12th Int. Conf. Texture of Materials, J.A. Szpunar (ed.), National Research Council of Canada (1999) pp. 1357-1362, incorporated in its entirety by reference herein).

SUMMARY OF THE PRESENT INVENTION

A feature of the present invention relates to high purity niobium and alloys thereof.

Another feature of the present invention is to provide a high purity niobium or alloys thereof exhibiting a fine grain structure and/or uniform texture.

Another feature of the present invention is to provide articles, products, and/or components containing the high purity niobium or alloys thereof.

An additional feature of the present invention is to provide processes to make the high purity niobium and alloys thereof as well as the articles, products, and/or components containing the high purity niobium or alloys thereof.

Additional features and advantages of the present invention will be set forth in part in the description that follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

To achieve these and other advantages, and in accordance with the purpose of the present invention, as embodied and broadly described herein, the present invention relates to niobium metal having a purity of at least 99.99% and more preferably at least 99.999%. The metal preferably has a fine grain structure and/or uniform texture.

The present invention further relates to an alloy containing niobium metal, wherein

the niobium metal present in the alloy has a purity of at least 99.99% and more preferably at least 99.999%. The alloy (e.g., at least the niobium metal present in the alloy or mixture) also preferably has a fine grain structure and/or uniform texture.

The present invention also relates to a high purity niobium metal or alloy suitable for use as a sputtering target, having a fully recrystallized grain size with an average grain size of about 150 μm or less and/or having a primary (111)-type texture substantially throughout the thickness of the niobium metal and preferably throughout the entire thickness of the niobium metal and/or having an absence of strong (100) texture bands within the thickness of the niobium.

The present invention further relates to manufacturing plate and sheet from the above-mentioned niobium metal by flat-forging the niobium metal, machining into rolling slabs, annealing rolling slabs, rolling into plate or sheet, then annealing the plate or sheet. Final products such as sputtering targets can be then machined from the annealed plate or sheet.

The present invention also relates to a sputtering target comprising the above-described niobium metal and/or alloy. The sputtering target can also be formed, for instance, by radial forging and subsequent round processing to produce billets or slugs, which are then forged and rolled to yield discs, which can then be machined and annealed.

The present invention further relates to barrier sheets, resistive films and capacitors comprising the above-described niobium metal and/or alloy.

The present invention also relates to articles, components, or products that comprise at least in part the above-described niobium metal and/or alloy.

Also, the present invention relates to a process of making the above-described niobium metal or alloy which involves reacting a salt-containing niobium metal either with or without the presence of an alloy metal salt (e.g. K_2TaF_7) with pure sodium or other suitable salt in a reactive container or pot and an agitator which both are made from or have

a liner comprising a metal or alloy thereof which has the same or higher vapor pressure as niobium metal at the melting point of niobium metal.

The present invention further relates to processing niobium metal powder or a blend of niobium metal and alloy powder by melting the powder in a high vacuum of 10^{-2} torr or more. The pressure above the melt is lower than the vapor pressures of the impurities existing in the powder melt stock. Preferably, the melting of the pure niobium or alloy metal powders are accomplished by electron beam melting.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention relates to a niobium metal having a purity of at least 99.99%. Preferably, the niobium metal has a purity of at least 99.999% and can range in purity from about 99.99% to about 99.999% or more. Other ranges include about 99.998% to about 99.999% and from about 99.999% to about 99.9995% and from about 99.999% to about 99.9999%. The present invention further relates to metal alloys that contain the high purity niobium metal of the present invention, such as a Nb-Ta alloy or other alloy which contains the high purity niobium as one of the components of the alloy.

The metallic impurities that may be present in the high purity niobium metal are less than or equal to 0.01% by weight and typically comprise other body-centered cubic (bcc) refractory metals of infinite solubility in niobium, such as tantalum, molybdenum, and tungsten. Similarly, the gaseous impurities that may be present in high purity niobium metal are less than or equal to 0.20% by weight and typically comprise interstitial gases such as oxygen, nitrogen, and carbon.

The niobium metal and alloys thereof containing the niobium metal preferably have a texture that is advantageous for particular end uses, such as sputtering. In other words, when the niobium metal or alloy thereof is formed into a sputtering target having a surface and then sputtered, the texture of the niobium metal in the present invention leads to a sputtering target which is easily sputtered and, very few if any areas in the sputtering target resist sputtering. Further, with the texture of the niobium metal of the present invention, the sputtering of the sputtering target leads to a very uniform sputtering erosion thus leading to a sputtered film which is therefore uniform as well. It is preferred that the niobium having any purity, but preferably a purity of at least about 99.99%, has a grain size of about 150 microns or less. More preferably, the grain size is from about 10 microns to about 150 microns, or from about 25 microns to about 100 microns. Preferably, the niobium metal is at least partially recrystallized, and more preferably at least about 80% of the niobium metal

is recrystallized and even more preferably at least about 98% of the niobium metal is recrystallized. Most preferably, the niobium metal is fully recrystallized.

Also, it is preferred that the niobium metal has a homogeneous texture through the thickness of the product. More preferably the texture is such that the (100) peak intensity within any 5% incremental thickness of the niobium is less than about 30 random, and/or has a natural log (Ln) ratio of (111):(100) center peak intensities within the same increment greater than about – 4.0 (i.e., meaning, -4.0, -3.0, -2.0, -1.5, -1.0 and so on) or has both the (100) centroid intensity and the ratio. The center peak intensity is preferably from about 0 random to about 30 random, and more preferably is from about 0 random to about 15 random. Other (100) centroid intensity ranges include, but are not limited to, from about 1 random to about 10 random and from about 1 random to about 5 random. Further, the log ratio of (111):(100) center peak intensities is from about – 4.0 to about 15 and more preferably from about –1.5 to about 7.0. Other suitable ranges of log ratios, include, but are not limited to, about –4.0 to about 10, and from about –3.0 to about 5.0. Most preferably, the niobium metal has the desired purity of at least about 99.99% and the preferred grain size and preferred texture with regard to the (100) incremental intensity and the (111):(100) ratio of incremental centroid intensities. The method and equipment that can be used to characterize the texture are described in Adams et al., Materials Science Forum, Vol. 157-162 (1994), pp. 31-42; Adams et al., Metallurgical Transactions A, Vol. 24A, April 1993-No. 4, pp. 819-831; Wright et al., International Academic Publishers, 137 Chaonei Dajie, Beijing, 1996 ("Textures of Material: Proceedings of the Eleventh International Conference on Textures of Materials); Wright, Journal of Computer-Assisted Microscopy, Vol. 5, No. 3 (1993), all incorporated in their entirety by reference herein.

The high purity niobium metal of the present invention can be used in a number of areas. For instance, the high purity niobium metal can be made into a barrier sheet for drawing superconductor filaments, a sputtering target, or into chemical energy (CE)

munition warhead liner. The high purity metal can also be used and formed into a capacitor anode or into a resistive film layer. The niobium metal or alloy of the present invention can be used in any article or component which conventional niobium or tantalum is used and the methods and means of making the various articles or components containing the conventional niobium can be used equally here in incorporating the high purity niobium metal into the various articles or components. For instance, the subsequent processing used in making sputtering targets, such as the backing plate, described in U.S. Patent Nos. 5,753,090, 5,687,600, and 5,522,535 can be used here and these patents are incorporated in their entirety by reference herein.

Generally, a process that can be used to make the high purity niobium metal of the present invention involves a refining process, a vacuum melting process, and a thermal mechanical process. In this process or operation, the refining process involves the steps of co-extracting the niobium metal, preferably in the form of a powder from salt containing niobium. The niobium powder, or co-reduced niobium metal and alloy powder, or a blend of niobium and elemental alloy powders, can then be subsequently vacuum melted.

After the refining process, the vacuum melting process is used to purge low melting point impurities, such as alkaline and transition metals from the niobium while consolidating the niobium material into a fully dense, malleable ingot. Preferably the niobium selected for melting has low amounts of impurities, especially, in the case of high-purity, low amounts of tantalum, molybdenum, and tungsten. More preferably, the amount of tantalum, molybdenum, and tungsten is below about 100 ppm, and most preferably is below about 10 ppm. Such a selection leads to a purer niobium cast metal. Then, after this process, a thermal mechanical process can be used which can involve a combination of cold working and annealing of the cast niobium to allow for material to recrystalize during annealing to achieve the preferred grain size and/or preferred texture in the finished product.

The high purity niobium metal preferably may be made by reacting a salt-containing niobium with at least one agent (e.g., compound or element) capable of reducing this salt to the niobium metal and further results in the formation of a slag and/or second salt in a reaction container. The reaction container can be any container typically used for the reaction of metals and should withstand high temperatures on the order of about 800°C to about 1,200°C. For purposes of the present invention, the reaction container or the liner in the reaction container, which comes in contact with the salt-containing niobium and the agent capable of reducing the salt to niobium, is made from a material having the same or higher vapor pressure as niobium at the melting point of the niobium. The agitator in the reaction container can be made of the same material or can be lined as well. The liner can exist only in the portions of the reaction container and agitator that come in contact with the salt and niobium. Examples of such metal materials which can form the liner or reaction container include, but are not limited to, metal-based materials made from nickel, chromium, iron, manganese, titanium, zirconium, hafnium, vanadium, ruthenium, cobalt, rhodium, palladium, platinum, or any combination thereof or alloy thereof as long as the alloy material has the same or higher vapor pressure as the melting point of niobium metal. Preferably, the metal is a nickel or a nickel-based alloy, a chromium or a chromium-based alloy, or an iron or an iron-based alloy. The liner, on the reaction container and/or agitator, if present, typically will have a thickness of from about .5 cm to about 3 cm. Other thicknesses can be used. It is within the bounds of the present invention to have multiple layers of liners made of the same or different metal materials described above.

The salt-containing niobium can be any salt capable of having niobium contained therein such as a niobium oxide (Nb_2O_5). With respect to the agent capable of reducing the salt to niobium and a slag in the reaction container, the agent which is capable of doing this reduction is any agent whose reaction products have a lower free-energy of formation (ΔG_f) than that of the niobium salt; for example, niobium can be fonned by a thermite reaction

between Nb_2O_5 and Al powder:

$$Nb_2O_5 + Al \rightarrow Nb + Al_2O_3$$

Other thermite reactants include, but are not limited to, magnesium, calcium, potassium, carbon, uranium, and thorium. With respect to the agent capable of reducing the salt to niobium and a second salt in the reaction container, the agent which is capable of doing this reduction is any agent which has the ability to result in reducing the salt-containing niobium to niobium metal and other ingredients (*e.g.* salt(s)) which can be separated from the niobium metal, for example, by dissolving the salts with water or other aqueous sources. Preferably, this agent is sodium. Other examples include, but are not limited to, lithium, magnesium, calcium, potassium, carbon, carbon monoxide, ionic hydrogen, and the like. Details of the reduction process which can be applied to the present invention in view of the present application are set forth in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edition, Vol. 22, pp. 541-564, U.S. Patent Nos. 2,950,185; 3,829,310; 4,149,876; and 3,767,456, all incorporated herein in their entirety by reference.

Once the niobium powder is extracted from this reaction, any impurities remaining, including any contamination from the reaction container can be removed through melting of the niobium powder. The niobium powder can be melted a number of ways such as a vacuum arc remelt and/or an electron beam melting. Generally, the vacuum during the melt will be sufficient to remove substantially any existing impurities from the recovered niobium so as to obtain high purity niobium. Preferably, the melting occurs in a high vacuum such as 10^{-4} torr or more. Preferably, the pressure above the melted niobium is lower than the vapor pressures of the metal impurities in order for these impurities, such as nickel and iron, to be vaporized. The diameter of the cast ingot should be as large as possible, preferably greater than 9 ½ inches. The large diameter assures a greater melt surface to vacuum interface that enhances purification rates. In addition, the large ingot diameter allows for a greater amount of cold work to be imparted to the metal during

processing, which improves the attributes of the final products. Once the mass of melted niobium consolidates, the ingot formed will have a purity of 99.99% or higher, and preferably 99.999% or higher. The electron beam processing preferably occurs at a melt rate of from about 150 to about 400 lbs. per hour using 20,000 to 40,000 volts and 15 to 40 amps, and under a vacuum of from about 1 X 10^{-3} to about 1 X 10^{-6} Torr. More preferably, the melt rate is from about 200 to about 300 lbs. per hour using from 24,000 to 26,000 volts and 17 to 36 amps, and under a vacuum of from about 1 X 10^{-4} to 1 X 10^{-5} Torr. With respect to the VAR processing, the melt rate is preferably of 500 to 1,500 lbs. per hour using 25-50 volts and 5,000 to 22,000 amps under a vacuum of 2 X 10^{-2} to 1 X 10^{-4} Torr, and more preferably 900 to 1200 lbs. per hour at from 30 to 50 volts and 16,000 to 18,000 amps, and under a vacuum of from 2 X 10^{-2} to 1 X 10^{-4} Torr.

The high purity niobium ingot can then be thermomechanically processed to produce the high purity niobium containing product. The fine and preferably fully recrystallized grain structure and/or uniform texture is imparted to the product through a combination of cold and/or warm working and in-process annealing. The high purity niobium product preferably exhibits a uniform texture of mixed or primary (111) throughout its thickness as measured by orientation imaging microscopy (OIM) or other acceptable means. With respect to thermomechanical processing, the ingot can be subjected to rolling and/or forging processes and a fine, uniform microstructure having high purity can be obtained. The high purity niobium has an excellent fine grain size and/or a uniform distribution. The high purity niobium preferably has an average recrystallized grain size of about 150 microns or less, more preferably about 100 microns or less, and even more preferably about 50 microns or less. Ranges of suitable average grain sizes include from about 25 to about 150 microns, from about 30 to about 125 microns, and from about 30 to about 100 microns.

The resulting high purity metal of the present invention, preferably has 100 ppm or

less metallic impurities and preferably 200 ppm or less O_2, 100 ppm or less N_2, and 100 ppm or less carbon. If a purity level of about 99.995 is desired, than the resulting high purity metal preferably has metallic impurities of about 50 ppm or less, and preferably 100 ppm or less O_2, 50 ppm or less N_2, and 50 ppm or less carbon.

With respect to taking this ingot and forming a sputtering target, the following process can be used. In one embodiment, the sputtering target made from the high purity niobium metal or alloy can be made by mechanically or chemically cleaning the surfaces of the niobium metal or alloy, wherein the niobium metal or alloy has a sufficient starting cross-sectional area to permit the subsequent processing steps described below. Preferably the niobium metal or alloy workpiece has a diameter of at least 9 ½ inches or more. The next step involves flat forging the niobium metal or alloy into one or more rolling slabs. The rolling slab(s) has a sufficient deformation to achieve substantially uniform recrystallization after the annealing step immediately following this step as described below. The rolling slab(s) is then annealed in vacuum and at a sufficient temperature to achieve at least partial recystallization of the rolling slab(s). The rolling slab(s) is then subjected to cold or warm rolling in both the perpendicular and parallel directions to the axis of the starting metal (e.g., the niobium metal or alloy ingot) to form at least one plate. The plate is then subjected to flattening (e.g., level rolling). The plate is then annealed a final time at a sufficient temperature and for a sufficient time to have an average grain size of equal to or less than about 150 microns and a texture substantially void of (100) textural bands. Preferably, no (100) textural bands exist. The plate can then be mechanically or chemically cleaned again and formed into the sputtering target having any desired dimension. Typically, the flat forging will occur after the niobium metal is placed in air for at least about 4 hours at temperatures ranging from ambient to about 370°C. Also, preferably before cold rolling, the rolling slabs are annealed at a temperature (e.g., from about 950°C to about 1500°C) and for a time (e.g., from about ½ hour to about 8 hours) to

achieve at least partial recrystallization of the niobium metal. Preferably the cold rolling is transverse rolling at ambient temperatures and the warm rolling is at temperatures of less than about 370°C.

With respect to annealing of the niobium plate, preferably this annealing is in a vacuum annealing at a temperature and for a time sufficient to achieve complete recrystallization of the niobium metal. The examples in this application set forth further preferred details with respect to this processing.

Another way to process the niobium metal or alloy metal into sputtering targets involves mechanically or chemically clean surfaces of the niobium metal (e.g., the niobium metal or alloy ingot), wherein the niobium metal has a sufficient starting cross-sectional area to permit the subsequent processing as described above. The next step involves round forging the niobium metal or alloy into at least one rod, wherein the rod has sufficient deformation to achieve substantially uniform recrystallization either after the annealing step which occurs immediately after this step or the annealing step prior to cold rolling. The niobium metal or alloy rod is then cut into billets and the surfaces mechanically or chemically cleaned. An optional annealing step can occur afterwards to achieve at least partial recrystallization. The billets are then axially forged into preforms. Again, an optional annealing step can occur afterwards to achieve at least partial recrystallization. However, at least one of the optional annealing steps or both are done. The preforms are then subjected to cold rolling into at least one plate. Afterwards, the surfaces of the plate(s) can be optionally mechanically or chemically clean. Then, the final annealing step occurs to result in an average grain size of about 150 microns or less and a texture substantially void of (100) textural bands, if not totally void of (100) textural bands. The round forging typically occurs after subjecting the niobium metal or alloy to temperatures of about 370°C or lower. Higher temperatures can be used which results in increased oxidation of the surface. Preferably, prior to forging the billets, the billets are annealed. Also, the preforms,

prior to cold rolling can be annealed. Preferably, these annealing temperatures will be from about 800°C to about 1300°C. Also, any annealing is preferably vacuum annealing at a sufficient temperature and for a sufficient time to achieve recrystallization of the niobium metal or alloy.

Preferably, the sputtering targets made from the high purity niobium have the following dimensions: a thickness of from about 0.080 to about 1.50", and a surface area from about 7.0 to about 1225 square inches, though other dimensions are possible.

The high purity niobium metal or alloy preferably has a primary or mixed (111) texture, and a minimum (100) texture throughout the thickness of the sputtering target, and is sufficiently void of (100) textural bands.

The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

WHAT IS CLAIMED IS:

1. Niobium metal having a purity of at least about 99.99%, and an average grain size of about 150 microns or less.

2. The niobium metal of claim 1, wherein said metal is fully recrystallized.

3. The niobium metal of claim 1, wherein said metal is at least partially recrystallyzed.

4. The niobium metal of claim 1, wherein about 98% or more of said metal is recrystallyzed.

5. The niobium metal of claim 1, wherein about 80% or more of said metal is recrystallyzed.

6. The niobium metal of claim 1, wherein said metal has a) a texture in which a (100) pole figure has a center peak intensity less than about 15 random or b) a log ratio of (111):(100) center peak intensities of greater than about –4.0, or c) both.

7. The niobium metal of claim 6, wherein said center peak intensity is from about 0 random to about 15 random.

8. The niobium metal of claim 6, wherein said center peak intensity is from about 0 random to about 10 random.

9. The niobium metal of claim 6, wherein said log ratio is from about –4.0 to about 15.

10. The niobium metal of claim 6, wherein said log ratio is from about –1.5 to about 7.0.

11. The niobium metal of claim 6, wherein said center peak intensity is from about 0 random to about 15 random, and said log ratio is from about –4.0 to about 15.

12. The niobium metal of claim 1, having a purity of from 99.995% to about 99.999%.

13. A metal alloy comprising the niobium metal of claim 1.

14. A metal alloy comprising the niobium metal of claim 3.

15. A metal alloy comprising the niobium metal of claim 6.

16. A sputtering target comprising the niobium metal of claim 1.

17. A sputtering target comprising the niobium metal of claim 3.

18. A sputtering target comprising the niobium metal of claim 6.

19. A capacitor comprising the niobium metal of claim 1.

20. A capacitor can comprising the niobium metal of claim 3.

21. A capacitor can comprising the niobium metal of claim 6.

22. A resistive film layer comprising the niobium metal of claim 1.

23. A resistive film layer comprising the niobium metal of claim 3.

24. A resistive film layer comprising the niobium metal of claim 6.

25. An article comprising at least as a component the niobium metal of claim 1.

26. An article comprising at least as a component the niobium metal of claim 3.

27. An article comprising at least as a component the niobium metal of claim 6.

28. Niobium metal having a) an average grain size of about 150 microns or less, or b) a texture in which a (100) pole figure has a center peak intensity equal to or less than about 30 random or c) a log ratio of (111):(100) center peak intensities of greater than about –4.0, or combinations thereof.

29. The niobium metal of claim 28 having an average grain size of from about 10 to about 100 microns.

30. The niobium metal of claim 28 having a ratio of (111):(100) center peak intensities of greater than about –4.0.

31. The niobium metal of claim 28, having both a) and b).

32. The niobium metal of claim 28, wherein said metal has purity of at least 99.99% niobium.

33. The niobium metal of claim 28, wherein said metal has a purity of 99.999% niobium.

34. The niobium metal of claim 28, wherein said metal is fully recrystallized.

35. The niobium metal of claim 32, wherein said metal is fully recrystallized.

36. The niobium metal of claim 33, wherein said metal is fully recrystallized.

37. The niobium metal of claim 28, wherein about 80% or more of said metal is fully recrystallized.

38. The niobium metal of claim 28, wherein said center peak intensity is from about 0 random to about 15 random.

39. The niobium metal of claim 28, wherein said log ratio is from about –4.0 to about 15.

40. An article comprising the niobium metal of claim 28.

41. An article comprising the niobium metal of claim 33.

42. A sputtering target comprising the niobium metal of claim 28.

43. A sputtering target comprising the niobium metal of claim 33.

44. A process for making the niobium metal of claim 1, comprising reacting a salt containing niobium and a metal salt with at least one agent capable of reducing the salt containing niobium to niobium in a reaction container having an agitator, wherein the reaction container or a liner in the reaction container and the agitator or a liner on the agitator are made from a metal material having the same or higher vapor pressure of niobium at the melting point of the niobium.

45. The process of claim 44, wherein the salt containing niobium comprises niobium oxide and the metal salt comprises potassium-tantalum fluoride and the agent comprises sodium.

46. The process of claim 45, further comprising adding at least one diluent salt comprising sodium fluoride and/or sodium chloride to said agitator.

47. The process of claim 44, wherein the reaction container or liner and the agitator or liner on the agitator are metal-based, wherein said metal is nickel, chromium, iron, manganese, titanium, zirconium, hafnium, vanadium, technetium, ruthenium, cobalt, rhodium, palladium, platinum, or any combination thereof.

48. The process of claim 47, wherein the metal is nickel or a nickel-based alloy.

49. The process of claim 47, wherein the metal is chromium or a chromium-based alloy.

50. The process of claim 47, wherein the metal is iron or an iron-based alloy.

51. The process of claim 44, further comprising recovering niobium by dissolving the second salt in an aqueous solution.

52. The process of claim 51, further comprising melting said recovered niobium and optionally said metal from said metal salt in a sufficient vacuum to remove substantially any existing impurities in said recovered niobium and obtain high purity niobium and optionally said metal.

53. The process of claim 52, wherein the vacuum is 10^{-4} torr or more.

54. The process of claim 52, wherein the pressure above the melted recovered niobium is lower than the vapor pressures of substantially all of the impurities.

55. The process of claim 52, wherein the impurities are removed by vaporization of the impurities.

56. The process of claim 52, wherein said melting is accomplished by electron beam melting.

57. The process of claim 52, wherein said melting is accomplished by vacuum arc remelt processing.

58. The process of claim 52, wherein the high purity niobium is allowed to form a solid and subjected to a rolling process, a forging process, or both.

59. The niobium metal of claim 1, wherein the niobium metal has a substantially fine and uniform microstructure.

60. The niobium metal of claim 1, wherein the niobium metal has an average grain size of from about 10 to about 150 microns.

61. The niobium metal of claim 1, wherein the niobium metal has an average grain size of from about 25 to about 100 microns.

62. The niobium metal of claim 1, wherein the niobium metal has an average grain size

of from about 25 to about 75 microns.

63. A process of making a sputtering target from niobium metal having a purity of at least 99.99%, comprising:

a) mechanically or chemically cleaning surfaces of the niobium metal, wherein the niobium metal has a sufficient starting cross-sectional area to permit steps b) through g);

b) flat forging the niobium metal into at least one rolling slab, wherein the at least one rolling slab has sufficient deformation to achieve substantially uniform recrystallization after annealing in step d);

c) mechanically or chemically cleaning surfaces of the at least one rolling slab;

d) annealing the at least one rolling slab at a sufficient temperature and for a sufficient time to achieve at least partial recrystallization of the at least one rolling slab;

e) cold or warm rolling the at least one rolling slab in both the perpendicular and parallel directions to the axis of the starting niobium metal to form at least one plate;

f) flattening the at least one plate; and

g) annealing the at least one plate to have an average grain size equal to or less than about 150 microns and a texture substantially void of (100) textural bands;

64. The process of claim 63, wherein the niobium metal has a purity of at least 99.999%.

65. The process of claim 63, wherein the flat forging occurs after the niobium metal is placed in air for at least about 4 hours and from temperatures ranging from ambient to about 1200°C.

66. The process of claim 63, wherein the cold rolling is transverse rolling at ambient temperatures and the warm rolling is at temperatures of less than about 370°C.

67. The process of claim 63, wherein the annealing of the plate is vacuum annealing at a temperature and for a time sufficient to achieve recrystallization of the niobium

metal.

68. A process of making a sputtering target from niobium metal having a purity of at least 99.995%, comprising:

a) mechanically or chemically cleaning surfaces of the niobium metal, wherein the niobium metal has a sufficient starting cross-sectional area to permit steps b) through i);

b) round forging the niobium metal into at least one rod, wherein the at least one rod has sufficient deformation to achieve substantially uniform recrystallization after annealing in step d) or step f);

c) cutting the rod into billets and mechanically or chemically cleaning the surfaces of the billets;

d) optionally annealing the billets to achieve at least partial recrystallization;

e) axially forging billets into preforms;

f) optionally annealing the preforms to achieve at least partial recrystallization;

g) cold rolling the preforms into at least one plate; and

h) optionally mechanically or chemically cleaning the surfaces of the at least one plate; and

i) annealing the at least one plate to have an average grain size equal to or less than about 150 microns and a texture substantially void of (100) textural bands, wherein annealing occurs at least in step d) or f) or both.

69. The process of claim 68, wherein the niobium metal has a purity of at least 99.999%.

70. The process of claim 68, wherein the round forging occurs after subjecting the niobium metal to temperatures of about 370°C or lower.

71. The process of claim 68 wherein prior to forging the billets, the billets are annealed.

72. The process of claim 68, wherein prior to cold rolling of the preforms, the preforms are annealed.

73. The process of claim 68, wherein the annealing of the preforms is vacuum annealing at a sufficient temperature and for a time to achieve recrystallization.